Precursors of Alk-2,4-dienals in Autoxidized Lard

Abstract

Evidence suggested that the low proportions of C_{10} alk-2,4-dienal found in mildly autoxidized linoleate or lard was basically due to a selective scission mechanism of the 13 and 9 conjugated linoleate hydroperoxide isomers. Spontaneous scission tended to be at the carbon linkage between a double bond and the hydroperoxide group. Thus the 13 hydroperoxide isomer produced the typically predominant amounts of hexanal. The 9 hydroperoxide isomer formed little C_{10} dienal and scission between the 9 and 10 carbons possibly led to some C_9 alk-2-enal. Earlier studies of free aldehyde formation by autoxidized oleate, linoleate, linolenate and arachidonate support such a scission mechanism. Autoxidized linoleate was decomposed by dilute acid to C_6 alkanal, some C_9 enal and no dienal. Under different stress, such as heat, alkaline conditions and Cu^{++}, large proportions of C_{10} dienals were formed. This appeared due to a shift in the point of scission to the saturated side of the hydroperoxide group.

Introduction

Alk-2,4-dienals have been found to contribute significantly to odors and flavor. Their formation and survival in food products therefore is of considerable importance and interest. The major aldehydes formed in autoxidized lard and pork adipose tissue stem from linoleic acid. These are C_6 alkanal, C_7, C_8, C_9 alk-2-enals and C_{10} alk-2,4-dienal. The theory of autoxidation of Farmer et al (9) predicts the formation of three hydroperoxides from linoleate. These are the C_9, C_{11} and C_{13} isomers. The C_9 and C_{13} isomers are the conjugated forms and Cannon (4) and Privett et al. (25) have shown that there was approximately 90% conjugation. A number of investigators (1,3,5,27) have reported isolating similar amounts of 9- and 13-hydroxy stearate after hydrogenation of the linoleate hydroperoxides. Despite this good evidence of the presence of equal amounts of the C_9 and C_{13} linoleate hydroperoxides, the aldehydes formed spontaneously do not suggest this. Invariably the major aldehyde formed in the autoxidation of lard or linoleate glyceride or ester is C_6 alkanal from the C_{13} hydroperoxide of linoleate. The quantity of C_{10} alk-2,4-dienal found is quite small and usually less than the predictably small C_7, C_8 and C_9 enal fractions. When the autoxidized lard or linoleate is heated at temperatures of 160 C and above, a considerable amount of alk-2,4-dienal is formed which frequently is greater than the C_6 alkanal. A precursor or the potential for C_{10} alk-2,4-dienal formation is therefore present. The possibility of change taking place during the reduction and hydrogenation steps to the hydroxy stearates apparently is ruled out by the work of Dolev et al. (5) with lipoxidase specific C_{13} linoleate hydroperoxide. This appeared to indicate that no change took place in the position of the hydroperoxide group during the $NaBH_4$ reduction treatment. An explanation of the anomalous circumstances surrounding C_{10} alk-2,4-dienal formation and its precursors would seem to require evaluation of the following. Alk-2,4-dienals oxidized faster than the unsaturated fatty acids, and this explains why the n-alkanals predominate in autoxidation although dienals are formed simultaneously. Dienals oxidize very rapidly separately, when exposed to light and air (22,28). However, this need not necessarily be the case in an autoxidizing fat system (21). The C_9 linoleate hydroperoxide is more stable than the C_{13} isomer. There appears to be no known reason why there should be a difference in stability in these hydroperoxides. An equilibrium may exist between the C_9 and C_{13} linoleate hydroperoxides with a predominance of the C_{13} isomer. Heating converts the C_{13} isomer to the C_9 isomer. A study by Gaddis et al. (15) suggested the possibility of such a mechanism.

The objective of this investigation was to contribute to the evaluation and possible explanations of the problem defined above, by studying the dienal stability in autoxidized fat and determining the monocarbonyl products obtained by various means of hydroperoxide decomposition.

Experimental Procedures

The rendered lard used in these investigations had been stored in vacuum packed cans at −30 F (−34.4 C). Tocopherol was removed from lard samples by passage through the Rota-film Molecular Still (A. F. Smith Co.), once at 40 ml/hr and 35 μ, or twice at 60 ml/hr and 35 μ. Solvents were purified as described by Schwartz et al. (26) and Gaddis et al. (14).

Fuller's and Infusorial earth in 15 g quantities were washed with five 200 ml portions of 6N HCl and filtered and washed with distilled water until the filtrate gave a clear solution with silver nitrate. The washed solids were dried in an oven at 150 C for 24 hr. Untreated Fuller's earth, Infusorial earth and Florisil were also dried in the oven under similar conditions. Nona-2,4-dienal prepared by the method of Pippen and Nonaka (24) was redistilled ($b_{1.5}$ 68°−70°) before use, and a stock solution of 0.140 g of dienal in 44.5 g of tocopherol-free lard prepared.

Lard samples were oxidized by spreading in a thin layer in 12 × 18 × 2½ in. pyrex dishes and storing in the dark at 20–40 C. Samples were protected by a covering sheet of parafilm (polyethylene). Contents were mixed on alternate days. An effort was made to obtain representative sampling and maintain a fairly constant thickness of lard. Duplicate 10 g lard samples were used.

In preliminary studies on monocarbonyl and dienal survival, carbonyls were isolated by steam distillation (11) and vacuum distillation (14).

The carbonyl 2,4-dinitrophenylhydrazones were fractionated as described by Gaddis et al. (14), and the monocarbonyl hydrazones separated into classes by the paper chromatographic method of Gaddis et al. (13). In the principal part of the work reported in this investigation, carbonyl 2,4-dinitrophenylhydrazones were isolated by the method of Schwartz et al. (26). The monocarbonyl derivatives were separated into classes by a modified method of
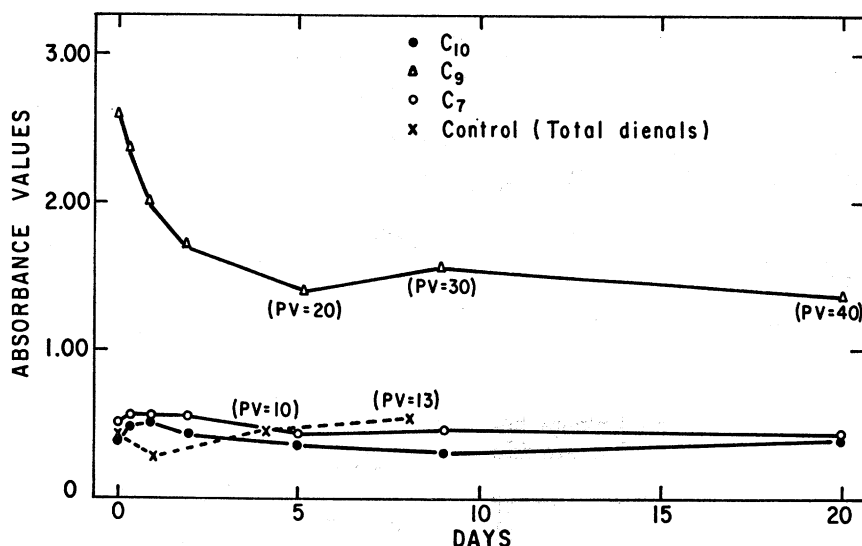
FIG. 1. Decrease in added C₉ dienal in lard oxidizing on celite.

Ellis and Gaddis (6). The modification consisted of the use of 11¼ × 12½ in. sheets stapled at the ends and solvent ascension for 1.5–2.0 hr. The resolved classes were separated into individual compounds by ascending thin layer chromatography on silica gel G (Brinkman) plates. The chromatograms were developed twice with hexane-benzene (1:3). The separated spots were removed and the solid was extracted exhaustively with chloroform. The chloroform was removed with a jet of nitrogen on the steam bath, and absorbance at λ max of the recovered monocarbonyl hydrazone in CCl₄ determined with a Cary Spectrophotometer. The thin layer method gave poor separation of aldehyde hydrazone homologues of carbon chain greater than C₇. These compounds were separated by the paper chromatographic methods of Ellis and Gaddis (6).

Some types of hydroperoxide breakdown were examined in sealed 20–30 ml tubes. In these experiments 0.5–1.0 g of oxidized lard or trilinolein samples was placed in the tube, metal stearates (1%) or acid washed Fuller's earth (10%) or other decomposing agent was added, and, after careful displacement of air with nitrogen, the tube was sealed off. The sealed tubes were heated in silicon oil at 85 (±2) C for 30 min with occasional swirling. The cooled contents of the tubes were dissolved in carbonyl-free hexane and made to 100 ml volume. Peroxide values (PV) (20) were determined on 10–20 ml aliquots. The remaining solution was reacted on the Schwartz column (26) to obtain carbonyl hydrazones.

Oxidized lard and trilinolein were also treated with metal chlorides under mild conditions. Weighed amounts (0.25–0.50 g) were dissolved in 10 ml carbonyl-free *t*-butyl alcohol and 2.0 ml H₂O, purged with N₂ for 3 min, treated with 0.3 g metal chloride in 2.0 ml H₂O, stoppered tightly, and agitated for 15 min to 3 hr at room temperature. Contents were diluted with 100 ml H₂O and extracted exhaustively with hexane. After drying the extract with anhydrous sodium sulfate, the volume was adjusted to 100 ml, the PV determined, and carbonyl 2,4-dinitrophenylhydrazones were isolated as previously described.

Results and Discussion
Alk-2,4-dienal Decomposition in Autoxidizing Fat

The rapid decomposition of alk-2,4-dienals when exposed alone to air and light has seemed to some investigators (22,29) sufficient explanation for the small amounts of free or spontaneously formed alk-2,4-dienals in certain autoxidized fats. In autoxidized linoleate there is ample evidence for the presence of approximately equal amounts of the conjugated 9- and 13-hydroperoxides (5). Everything else being equal, as much C₁₀ alk-2,4-dienal should be present as C₆ alkanal, but this is definitely not the case.

Lillard and Day (22) compared the rates of oxygen absorption of nonanal, non-2-enal, hepta-2,4-dienal, methyl linoleate and linolenate. Hepta-2,4-dienal and non-2-enal were almost equally susceptible and more sensitive to oxidation than linoleate and linolenate. On the basis of these individual oxidations, added dienal might well have disappeared before fatty acid oxidation was initiated. The behavior of the three aldehyde classes in the presence of oxidizing esters and triglycerides of unsaturated fatty acids has not been determined.

Studies indicated some degree of stability of dienals in autoxidizing lard. All aldehyde classes decreased, but the rate of dienal loss seemed no greater than the alkanals. Figure 1 shows the change in concentration of added C₉ dienal with degree of autoxidation of tocopherol-free lard. Added C₉ dienal in all experiments showed an initial rapid decrease which may have corresponded to an induction period or an initial onset of oxidation. When peroxide values reached the neighborhood of 20, the rate of C₉ dienal disappearance decreased. In all such experiments, there was little change in the amount of C₇ and C₁₀ alk-2,4-dienals present.

In general, the data indicate some loss of dienal through or concurrent with fat oxidation. However, there was a leveling off of dienal loss, even though the lard was oxidizing at an accelerating rate. The decrease in dienal loss at the concentrations employed is considered significant since dienal formation during lard autoxidation is extremely gradual (14). In some experiments, added dienal appeared to affect oxidation rates. It appears that dienal loss is too gradual to completely account for the extremely minor proportions of alk-2,4-dienals normally present

in oxidized lard. The results are not considered absolutely conclusive, and further investigation with pure unsaturated fatty acid esters would be appropriate. However, other data make this unnecessary.

Considerable quantities of C_7, C_8 and C_9 alk-2-enals are always present among the free aldehydes (8,14). These compounds are definitely products of linoleate autoxidation and apparently are derived from minor primary oxidation products and by obscure mechanisms. The 2-enals, although nearly as sensitive to oxidation, considerably exceeded C_{10} dienal (and C_9 dienal) which ensues from a major linoleate hydroperoxide isomer.

Hydroperoxide Decomposition

Autoxidation is propagated by hydroperoxide decomposition, but the relatively small amount of free aldehyde (7,8,13–16) makes it appear that monocarbonyl formation is a minor part of the mechanism. Some methods of isolation of monocarbonyl compounds (7,8,15,16) form aldehydes in the process. However, in most of the procedures the composition of these aldehydes indicated little breakdown of the 9-linoleate hydroperoxide to C_{10} dienal. Heating at around 165 C produced a high proportion of C_{10} dienal. Unusual results were obtained with the Pool and Klose method (15) of reaction with 2,4-dinitrophenylhydrazine on alumina. High dienal proportions were obtained, and in the case of linoleate this was characterized by large amounts of the unusual C_9 alk-2,4-dienal. Results with alumina as a hydroperoxide decomposer may be interpreted (7,18) in a number of different ways, and in addition, nothing conclusive has been demonstrated by them. It may be said that reactions of the C_9 linoleate hydroperoxide are complex and quite different from those of the C_{13} linoleate hydroperoxide.

Acid breaks down hydroperoxides (18) and forms monocarbonyl compounds (2,8,14) in the process. Horikx (18) reported almost quantitative conversion of oxidized methyl oleate to carbonyls when optimum amounts of the hydroperoxide were applied to the celite dinitrophenylhydrazine hydrochloric acid column. As used in general applications, quantitative performance of the method is sensitive to overloading by oxidized material (8). No dienal was formed from oxidized linoleate, but large amounts of C_6 hexanal were released.

There is considerable literature (17) on various means for decomposition of hydroperoxides. However, nothing has been reported on the effect of different agents on the carbonyls formed from autoxidized unsaturated fatty acids. The results of warming autoxidized lard at 85 C in a sealed tube with metal stearates, a naphthenate, and acidic and basic agents is shown in Table I. Among the ions examined, Cu^{++} showed the greatest decrease in PV and Fe^{++} the least, and this was reflected by a direct relationship in amount of aldehyde. Cu^{++}, Fe^{++}, Mn^{++} and MgO showed increases in the proportion of alk-2,4-dienals. Co^{++} and Sn^{++} had dienal proportions similar to the control. Stannous ion (Sn^{++}), a useful reducing agent, exhibited considerable monocarbonyl formation (8). No dienals were formed by the hydroperoxide decomposition promoted by acid-washed Fuller's earth. The hydroperoxides were completely broken down and 17% were converted to monocarbonyls. When C_9 dienal was added to an oxidized fat prior to acid-washed Fuller's earth

TABLE I

Effect of Various Agents on Oxidized Lard in Sealed Tubes at 85 C

| Agent | PV meq/1000 g decrease | Monocarbonyl | | | | |
		μm/10 g	Per cent PV conversion	Alkanal %	Dienal μm/10 g	Dienal %
Control PV 130	— 5	3.8		65	0.25	7
Co^{++} stearate	—115	46.1	8.0	75	3.23	7
Cu^{++} stearate	—120	60.5	10.0	59	13.31	22
Fe^{++} stearate	— 25	9.4	7.5	52	1.60	17
Sn^{++} stearate	— 85	20.0	3.2	75	1.40	7
Mn^{++} stearate	—115	54.3	9.0	64	5.97	11
Cu^{++} naphthenate[a]	?	34.7	?	56	7.29	21
Florisil	— 50	7.1	2.8	48	0.78	11
MgO	— 65	10.4	3.2	42	2.95	24
Fuller's earth (acid washed)	—130	112.7	17.3	76	0.00	0

[a] Soluble in nonpolar solvents which prevents PV measurement.

treatment, it was recovered quantitatively. The agent or conditions therefore were not dienal destructive. Cupric ion (Cu^{++}) is well known as a powerful specific decomposer of hydroperoxides. The relatively high proportion of dienal formed is significant, but on the other hand the released monocarbonyls represent less than 10% of the hydroperoxides decomposed.

The data indicate the presence of a considerable amount of dienal precursors, yet by use of acid conditions complete hydroperoxide breakdown can be obtained with no dienal formation. There is not sufficient evidence to determine whether the differences are due to different mechanisms of scission of the hydroperoxide isomers, a hypothetical equilibrium between hydroperoxide isomers, or to different stabilities of the carbonyl precursors.

The effect of metal chlorides on autoxidized lard in 70% aqueous t-butyl alcohol was examined. Earlier work had indicated considerable oxidation by Cu^{++}, Sn^{++} and Fe^{++} chlorides of several different classes of alcohol. In this case acetone was formed. The three salts effectively removed the hydroperoxides. Sn^{++} formed an appreciable amount of aldehyde, but conversion from hydroperoxide was relatively low at about 2%. As shown in Table II, aldehyde analyses (corrected for acetone) for $CuCl_2$ and $FeCl_2$ were somewhat similar and low in alk-2,4-dienals. Conversions of hydroperoxide to monocarbonyls were 13% and 20%, respectively. The data indicate an effect by polar conditions on hydroperoxide decomposition and conversion to aldehydes.

TABLE II

Effect of Metal Chloride-70% Tertiary Butyl Alcohol Hydroperoxide Decomposition on Distribution of Individual Aldehydes

| Lard, PV 130 | CuCl₂ Per cent PV conversion | Monocarbonyl | | FeCl₂ Per cent PV conversion | Monocarbonyl | |
		μm/10 g	%		μm/10 g	%
Total	13.5	87.99		20.6	133.6	
Alkanals						
C_1, C_2		5.08	5.8		7.47	5.6
C_3		10.00	11.4		14.88	11.1
C_5		15.03	17.1		......	......
C_6		35.04	39.8		69.98	52.4
$C_9 > C_9$		......	......		7.47	5.6
Alk-2-enals						
C_4		1.24	1.4		0.55	0.4
C_5		2.48	2.8		2.77	2.1
C_6		......	......		3.31	2.5
C_7		2.51	2.9		3.31	2.5
C_8		2.51	2.9		3.31	2.5
C_9		1.24	1.4		1.64	1.2
C_{10}		2.48	2.8		5.57	4.2
C_{11}		2.48	2.8		5.57	4.2
Alk-2,4-dienals						
C_7		2.73	3.1		4.10	3.1
C_{10}		1.85	2.0		3.67	2.6

Monocarbonyl From Autoxidized Trilinolein on Treatment in Sealed Tubes

Monocarbonyl	Fuller's earth acid washed 85 C			Cupric stearate 85 C		Heated			
						165 C		175 C	215 C
	PV 50	PV 65	PV 180	PV 50	PV 65	PV 50	PV 65	PV 180	PV 180
Total μm/10 g	87.72	77.73	199.8	12.01	18.32	28.0	33.99	116.7	139.4
Per cent PV conversion	35.1	23.9	22.2	4.8	5.6	11.2	10.5	13.0	15.5
Alkanals, %									
C_5	12		10	5	5	2	2	27	30
C_8	53	70	64	23	26	9	13	16	19
$C_9 > C_9$	2	2	1			..	....		
Enals, %									
C_6			2	5	2	8	2	4	4
C_7	1	2		12	13	15	17	19	16
C_8	1	..		1	2	....	....	1	1
C_9	31	26	23	..	7	6	8	3	4
Dienals, %									
C_9	....	....	....					2	2
C_{10}	....	....	....	54	45	60	58	43	43

Decomposition studies were made on autoxidized trilinolein since it is the fatty acid that is specifically involved in the problem. Table III includes a summation of results of comparisons in sealed tubes at several levels of autoxidation. The data were as might have been predicted from the performance of the autoxidized lard. Fuller's earth gave a remarkably high conversion of hydroperoxides to monocarbonyls considering the complexities of the reactions involved. An average of 62% was C_6 alkanal. The relatively high proportion of C_9 alk-2-enal may be highly significant in view of the absence of C_{10} alk-2,4-dienal. The formation of C_9 enal as the major enal is characteristic of acid conditions, and this is in interesting contrast with certain methods of free aldehyde isolation (8).

Cupric stearate, although effective in hydroperoxide decomposition had a comparatively low conversion to aldehydes. However, these monocarbonyls were similar in quantitative class composition to those of the heated samples. Amounts of C_6 alkanal as a result of cupric stearate and heat treatment were similar, and the data indicate little increase by these processes. There was therefore small scission of the C_{13} linoleate hydroperoxide in the usual sense. The major alk-2-enal was C_7; this approached the size of the C_6 alkanal fraction. A high proportion of C_{10} alk-2,4-dienal was formed; this should have come from the C_9 linoleate hydroperoxide or some unstable intermediate. The association between a C_7 alk-2-enal and a product of a C_9 linoleate conjugated hydroperoxide on one hand, and a C_{13} linoleate conjugated hydroperoxide scission product and a C_9 alk-2-enal may contain a clue to the mechanisms involved.

A comparison is shown in Table IV of reduction by $FeCl_3$ in tertiary butyl alcohol and Fuller's earth

TABLE IV

Effect of Ferrous Ion in a Polar Solvent on the Decomposition of Trilinolein Hydroperoxide

Peroxide 70	Monocarbonyls			
	FeCl₂ in tert. butyl alcohol		Fuller's earth acid washed 85 C sealed tube	
	μm/10 g	%	μm/10 g	%
Total	10.12		111.99	
Conversion PV		2.9		32
Alkanal	4.30	43	82.18	74
C_6	2.98	30	79.84	72
Enals	2.98	29	29.81	26
C_7	1.27	13	1.49	1
C_8	0.22	2		
C_9	0.51	5	28.32	25
Alk-2,4-dienals	2.84	28		
C_{10}	2.84	28		

treatment in a sealed tube at a fairly low peroxide level. Conversion of hydroperoxides by Fe^{++} to monocarbonyls was only 2.9%. There was great contrast in the quantitative composition of the aldehydes released by the two procedures. The balance between C_6 alkanal and C_{10} alk-2,4-dienal and the fact that C_7 alk-2-enal is the major enal are noteworthy effects of the $FeCl_2$ treatment. In similar treatment of oxidized lard, hydroperoxide conversion was much higher.

Mechanism Speculations

Swoboda and Lea (28) have also noted the relationships between C_6 alkanal and C_{10} dienal formed by linoleate during low temperature autoxidation and the effect of thermal decomposition. The fact that both compounds arise from positional isomers of conjugated linoleate hydroperoxide was not considered to agree with quantitative aspects and accepted mechanisms. However, these investigators (28) considered the best explanation was a selective further oxidation of dienals during autoxidation.

The data accumulated in the present research seem to make the above conclusion untenable. It is doubtful that the oxidative susceptibility of the dienals accounts for their low content in autoxidized lard or linoleate. Aside from the considerations demonstrated, fairly substantial amounts of C_7 dienal are present in the volatile aldehydes of autoxidized linolenate (8,13) although at least four conjugated linolenate hydroperoxides are present. This is not noticeable in autoxidized lard because of the low linolenic acid content. In autoxidized linoleate, vigorous conditions are necessary for formation of C_{10} alk-2,4-dienal. In autoxidation of linoleate at moderate temperatures, scission was mastly of the 13 linoleate hydroperoxide between the double bond and the peroxide group to form C_6 alkanal in the accepted way. This scission represented only a small part of the total hydroperoxides decomposed in the spontaneous course of autoxidation. In directed decomposition of linoleate and lard hydroperoxides the total conversion to volatile monocarbonyls was usually small. Rather excellent conversion (Fuller's earth) was obtained with mineral acid, but this resulted in no dienal. The 9 linoleate hydroperoxide, unless subjected to stress, seems to break down in a complex way.

The fact is that, while the free-radical chain reaction mechanism for autoxidation of unsaturated fatty acids has been well established, there is not much evidence concerning the scission of hydroperoxides to volatile monocarbonyls. A reaction

frequently postulated is the breakdown of the hydroperoxide into hydroxy- and alkoxy-free radicals, the latter then undergoing scission of the carbon-carbon bond adjacent to the carbonyl group. As shown in Diagram A, two types of scission may occur.
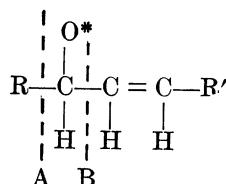
$$R-\overset{\overset{\displaystyle O^*}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{}{\underset{\underset{\displaystyle H}{|}}{C}}=\overset{}{\underset{\underset{\displaystyle H}{|}}{C}}-R'$$

A B

Diagram A

(R and R' may be the methyl or carboxyl end of the fatty acid.)

In the case of oleate with four isomeric hydroperoxides, 8, 9, 10 and 11 hydroperoxy monoenes, the aldehydes formed by type A cleavage would be C_{10} and C_{11} enals, and by type B cleavage C_8 and C_9 alkanals. When oleate is oxidized at moderate temperatures, the spontaneously formed major monocarbonyls are mostly saturated (8). Therefore, the type B scission next to the double bond takes place most readily. Heating or more vigorous isolation methods can produce large proportions of enal compounds (8,13). In all of the autoxidized fatty acid studies (7,8,13), including oleate, linoleate, linolenate and arachidonate, the spontaneously formed aldehydes are mostly alkanals. Horvat et al. (19) examined the volatile products from the autoxidation of methyl linoleate at 22 C. Besides alkanals a number of components such as esters, dioxalones, alcohols, ketones, hydrocarbons and acetals were found. However, no unsaturated monocarbonyl compounds were detected. Thus, the C-C linkage between a peroxide group and a double bond is the most vulnerable to scission and the peroxide group must be included in the volatile fragment to obtain a carbonyl group. The present work indicates that the scission of hydroperoxides may be guided by such a general behavior.

Loury and Prevot (23), as shown in Diagram B, have similarly described a dual scission of 13 linoleate hydroperoxide in which either hexanal or pentanol can be formed.

```
        A   B
        | 13 | 12
        |    |
CH3—(CH2)4—CH—CH = CH—CH = CH—(CH2)7COOH
        |    |
        | O  |
        |- - -|
       / | O |  \
      /  | H |   \
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Scission 13–14   Scission 12–13 to form
with fixation   n-hexanal
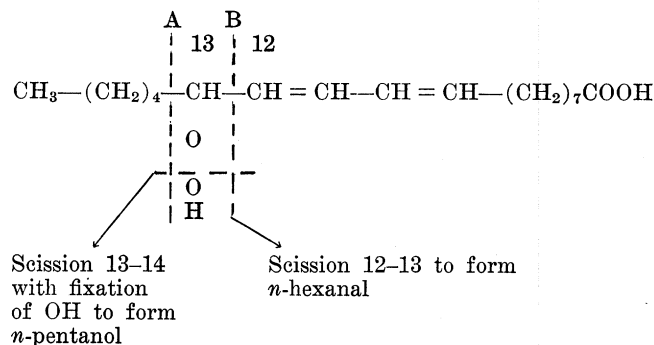of OH to form
n-pentanol

Diagram B

Reference has been made above to the moderately large amounts of alk-2-enal formed in the autoxidation of linoleate even though such compounds are sensitive to oxidation (22). Where these compounds are formed spontaneously, the free enals (C_7, C_8, C_9) do not differ greatly in amount although there is some tendency for C_7 or C_8 to be the major enal. In the decomposition of linoleate hydroperoxide with

acid-washed Fuller's earth, the principal monocarbonyls were C_6 alkanal and C_9 enal with the $C_6:C_9$ ratio being greater than 2:1. The precursors of C_9 enal are in doubt. The relatively large amount of the enal formed tends to eliminate the nonconjugated 10 linoleate hydroperoxide as the primary precursor. It may be possible that the precursor of C_9 enal is the 9-linoleate hydroperoxide and formed as indicated in Diagram C.

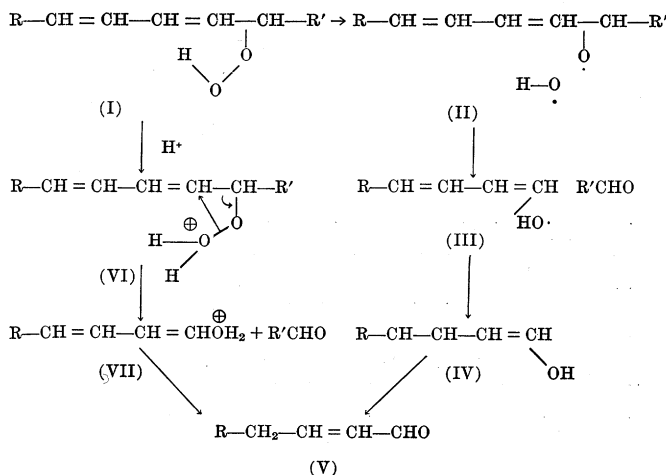$$R-CH = CH-CH = CH-CH-R' \rightarrow R-CH = CH-CH = CH-CH-R'$$

Diagram C

(where R is methyl and R' is carboxyl end of fatty acid)

A 1,3-dienyl radical (II) is formed and this undergoes a type B scission of the carbon chain as set forth by Swoboda and Lea (28) and above. The (III) fragment reacts with hydroxyl radical to give (IV) and thereafter subsequent enolization and isomerization of the 3-enal to the C_9 enal. Transformations between (II) and (IV) would need to be rapid while the .OH radical is in close proximity. The protonated hydroperoxide (VI) by a concerted process (VI → VII) can likewise be converted to (V). Acid favors the C_9 enal formation. Vigorous conditions such as heating with or without Cu++ produce C_{10} dienal and C_7 enals as the major compounds. The course of breakdown of linoleate hydroperoxides obviously differs according to conditions. Under mild conditions, in the course of normal progressive autoxidation, selectivity is exhibited in the formation of monocarbonyls with the least amount of conjugation and unsaturation. This is also the case in decomposition of acid conditions.

A curious effect of the type of hydroperoxide decomposition on the λ max of the polar 2,4-dinitrophenylhydrazones was noted. This fraction was retained by hydrated alumina and eluted with chloroform. Polar hydrazones from Fuller's earth treatment had a low λ max while those from Cu stearate or heating procedures had a high λ max of about 379. Little has been determined concerning the nature of the polar carbonyls except the report of Frankel et al. (10) on evidence for the presence of aldehyde-glycerides. The significance of the above observation can therefore not be evaluated.

The data discussed suggest the following tentative conclusions. The low concentration of C_{10} alk-2,4-dienal found in linoleate dominant fats under moderate conditions of autoxidation appear to be due to a selective course of scission of the hydroperoxides. The point of scission tends to be at the carbon linkage between a double bond and the hy-

droperoxide group. Thus, the 13 linoleate hydroperoxide yields predominant amounts of hexanal. The 9 linoleate hydroperoxide forms little C_{10} dienal spontaneously and with scission between the 9 and 10 carbons may form some C_9 enal. Under stress, such as heat, alkali, or Cu^{++} decomposition, scission takes place at the 9–8 carbons to yield C_{10} dienal. There is also some evidence that scission of the 13 linoleate hydroperoxide may be changed by vigorous conditions which promote splitting between the 13 and 14 carbons. Consideration of previous studies with oleate, linolenate and arachidonate also suggests that there may be a general strong tendency for scission to take place at the carbon linkage between the hydroperoxide group and a double bond.

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